

DMDO/DEG-DVE Polythioether	100
Calcium carbonate	60
Magnesium oxide	1
Phenolic resin	1
DMP-30	1
Isopropyl alcohol	3

The compounded polymer was mixed intimately with the epoxy resin curing agent of Examples 9-11 above, in the weight ratio of 10:1 and cured at ambient temperature and humidity. The following physical properties were obtained for the cured composition:

Cure hardness at 25° C.	60 Shore A
Tensile strength at break	550 psi
Elongation at break	600%
Notched tear strength	100 p/i
Low-temperature flexibility (AMS 3267 § 4.5.4.7)	passed

Example 15

Sealant Composition

A sealant composition including the ECHDT/DEG-DVE polythioether polymer of Example 9 was compounded as follows (amounts in parts by weight):

ECHDT/DEG-DVE Polythioether	100
Calcium carbonate	54
Hydrated aluminum oxide	20
Magnesium oxide	1
Phenolic resin	1
Hydrogenated terphenyl plasticizer	6
DMP-30	1
Isopropyl alcohol	3

The compounded polymer was mixed intimately with an epoxy resin curing agent in the weight ratio of 10:1 and cured at ambient temperature and humidity. The following physical properties were obtained for the cured composition:

Cure hardness at 25° C.	72 Shore A
Tensile strength at break	550 psi
Elongation at break	450%
Notched tear strength	85 p/i
Low-temperature flexibility	passed

Example 16

OH-Terminated Capped Polythioether

In a 500 ml flask, 275.9 g (1.09 mol) PLURIOL® E-200 divinyl ether, 174.7 g (0.95 mol) DMDO, 28.7 g (0.30 mol) 3-mercaptopropanol and 1.83 g (7.3 mmol) TAC were mixed. The mixture was heated to 70° C., and 2.3 g (12 mmol) VAZO® 67 were added slowly. The reaction mixture was stirred and heated at 85-90° C. for 4 hours to afford 480 g (0.15 mol, yield 100%) of a polymer having an equivalent weight of 1670 (number average molecular weight=3200, functionality F=2.05).

Example 17

OH-Terminated Capped Polythioether

In a 250 ml flask, 104.72 g (0.57 mol) DMDO, 80.73 g (0.51 mol) DEG-DVE and 14.96 g (0.13 mol) butanediol

monovinyl ether were mixed and heated to 75° C. To the heated mixture 0.60 g (3 mmol) VAZO® 67 were added slowly. The reaction mixture was stirred and heated at 75-85° C. for 6 hours to afford 200 g (0.064 mol, yield 100%) of a clear, nearly colorless polymer with very low odor and a viscosity of 79 poise at 20° C. The equivalent weight was 1570 (number average molecular weight=3200, functionality F=2.00).

Example 18

Vinyl-Terminated Polythioether

In a 250 ml flask, 97.63 g (0.53 mol) DMDO, 97.66 g (0.62 mol) DEG-DVE and 5.31 g (0.21 mol) TAC were mixed and heated to 70° C. To the heated mixture 0.80 g (4 mmol) VAZO® 67 were added slowly. The reaction mixture was stirred and heated at 85-90° C. for 4 hours to afford 200 g (0.11 mol, yield 100%) of a low-odor polymer having a T_g of -68° C. and a viscosity of 25 poise at 20° C. The equivalent weight was 1570 (number average molecular weight=1900, functionality F=2.2).

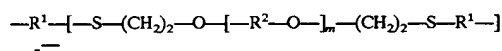
Example 19

Ethyl Vinyl Ether-Terminated Polythioether

In a 100 ml flask, 43.05 g (0.24 mol) DMDO, 34.22 g (0.22 mol) DEG-DVE and 2.84 g (0.04 mol) ethyl vinyl ether were mixed and heated to 80° C. To the heated mixture 0.28 g (1.5 mmol) VAZO® 67 were added slowly. The reaction mixture was stirred and heated at 85° C. for 6 hours to afford 80 g (0.02 mol, yield 100%) of a polymer having a T_g of -67° C. and a viscosity of 64 poise at 20° C. (number average molecular weight=4100, functionality F=2.0).

What is claimed is:

1. A polythioether comprising a structure having the formula I



wherein

R^1 denotes a divalent C_{2-6} n-alkyl, C_{3-6} branched alkyl, C_{6-8} cycloalkyl or C_{6-10} alkylcycloalkyl group, $\text{—}[(\text{—CH}_2\text{—})_p\text{—X—}]_q\text{—}[(\text{—CH}_2\text{—})_r\text{—}]$, or $\text{—}[(\text{—CH}_2\text{—})_p\text{—X—}]_q\text{—}[(\text{—CH}_2\text{—})_r\text{—}]$ in which at least one $\text{—CH}_2\text{—}$ unit is substituted with a methyl group,

R^2 denotes methylene, a divalent C_{2-6} n-alkyl, C_{2-6} branched alkyl, C_{6-8} cycloalkyl or C_{6-10} alkylcycloalkyl group, $\text{—}[(\text{—CH}_2\text{—})_p\text{—X—}]_q\text{—}[(\text{—CH}_2\text{—})_r\text{—}]$ or $\text{—}[(\text{—CH}_2\text{—})_p\text{—X—}]_q\text{—}[(\text{—CH}_2\text{—})_r\text{—}]$ in which at least one $\text{—CH}_2\text{—}$ unit is substituted with a methyl group,

X is one selected from the group consisting of O, S and $\text{—NR}^6\text{—}$,

R^6 denotes H or methyl,

m is a rational number from 0 to 10,

n is an integer from 1 to 60,

p is an integer from 2 to 6,

q is an integer from 1 to 5, and

r is an integer from 2 to 10,

said polythioether being a liquid at room temperature and pressure.

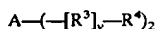
2. The polythioether of claim 1 which has a glass transition temperature T_g not higher than -50° C.

3. The polythioether of claim 1 which, when cured, has a % volume swell not greater than 25% after immersion for one week in JRF type 1 at 60° C. and ambient pressure.

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4. The polythioether of claim 1 which has a number average molecular weight between about 500 and 20,000.

5. The polythioether of claim 1 having the formula II



wherein

A denotes a structure having the formula I,

y is 0 or 1,

R³ denotes a single bond when y=0 and $-S-(CH_2)_2-$ 10
 $[-O-R^2-]_m-O-$ when y=1,

R⁴ denotes $-SH$ or $-S-(CH_2)_2-O-R^5$ when
y=0 and $-CH_2=CH_2$ or $-(CH_2)_2-S-R^5$ when
y=1,

R⁵ denotes C₁₋₆ n-alkyl which is unsubstituted or substituted with at least one $-OH$ or $-NHR^7$ group, and 15

R⁷ denotes H or a C₁₋₆ n-alkyl group.

6. The polythioether of claim 5 wherein y=0.

7. The polythioether of claim 6 wherein R⁴ is $-SH$. 20

8. The polythioether of claim 7 wherein (i) when m=1 and R²=n-butyl, R¹ is not ethyl or n-propyl, and (ii) when m=1, p=2, q=2, r=2 and R²=ethyl, X is not O.

9. The polythioether of claim 6 wherein R⁴ is $-S-(CH_2)_2-O-R^5$.

10. The polythioether of claim 9 wherein R⁵ is n-C₂H₅,
n-C₄H₉-OH or n-C₃H₇-NH₂.

11. The polythioether of claim 5 wherein y=1.

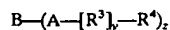
12. The polythioether of claim 11 wherein R⁴ is $-CH=CH_2$.

13. The polythioether of claim 11 wherein R⁴ is $-(CH_2)_2-S-R^5$.

14. The polythioether of claim 13 wherein R⁵ is n-C₃H₇-OH.

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15. The polythioether of claim 1 having the formula III



III

II 5 wherein

A denotes a structure having the formula I,

y is 0 or 1,

R³ denotes a single bond when y=0 and $-S-(CH_2)_2-$
 $[-O-R^2-]_m-O-$ when y=1,

R⁴ denotes $-SH$ or $-S-(CH_2)_2-O-R^5$ when
y=0 and $-CH_2=CH_2$ or $-(CH_2)_2-S-R^5$ when
y=1,

R⁵ denotes C₁₋₆ n-alkyl which is unsubstituted or substituted with at least one $-OH$ or $-NHR^7$ group,

R⁷ denotes H or a C₁₋₆ n-alkyl group,

z is an integer from 3 to 6, and

B denotes a z-valent residue of a polyfunctionalizing agent.

16. The polythioether of claim 15 wherein z=3.

17. The polythioether of claim 16 which has an average functionality from about 2.05 to 3.00.

18. The polythioether of claim 15 wherein y=0.

19. The polythioether of claim 18 wherein R⁴ is $-SH$.

20. The polythioether of claim 18 wherein R⁴ is $-S-(CH_2)_2-O-R^5$.

21. The polythioether of claim 15 wherein y=1.

22. The polythioether of claim 21 wherein R⁴ is $-CH=CH_2$. 30

23. The polythioether of claim 21 wherein R⁴ is $-(CH_2)_2-S-R^5$.

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